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Glaciochemical investigations on the subterranean ice deposit of Vukušić Ice Cave, Velebit Mountain, Croatia

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Abstract

The ^{3}H activity, $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratio and concentration of 33 metals and metalloids have been analysed on ice core samples from the perennial subterranean cave ice deposit of Vukušić Ice Cave, Velebit Mt. The tritium data suggested that the ice deposition at 2–2.4 m depth is build from precipitation fallen ~ 45 years before sampling and the uppermost ice layer could be estimated between early 1970s and early 1980s or between ~ 1954 and 1960. Both the fluctuation range of stable water isotopes and the derived isotopic waterline of the ice agree reasonably well with the corresponding data of the local precipitation. This fact predicts that the potential of Vukušić Ice Cave's ice deposit is superior for paleoclimatological studies to the nearby Ledena Pit. Principal component analysis helped to select three groups of elements. The Ca-Mg governed group (PC1) encompasses the bedrock related components; hence the fluctuation of these elements might reflect the past intensities of the dissolution process of the adjacent epikarst. The Zn governed group (PC2) preserves probably an atmospheric deposition signal and related to the emission of regional non-ferrous metallurgy. PC3 is governed by Al and Fe. This probably carries the distal, non-karstic crustal signal hence might be related to the past atmospheric circulation (i.e. wind direction and speed).

1 Introduction

In the recent decade scientific interest devoted to the small glacier and glacierets of the Mediterranean region has intensified owing to their sensitive response to the regional climatic changes over the past ~ 200 yr (González Trueba et al., 2008; Grünewald and Scheithauer, 2010).

Dramatic degradation has been reported on these ice bodies from the Iberian Peninsula (Chueca et al., 2005; González Trueba et al., 2008) through the Apennines (Citterio et al., 2007; D'Orefice et al., 2000) and the Balkans (Gabrovec, 1998; Grünewald

et al., 2006; Hughes, 2007, 2008, 2009; Pavšek, 2007, 2010) or from Asia Minor (Sarıkaya et al., 2009) compared to their extension in the late 19th and early 20th century. Usually less known is that perennial subterranean ice deposits have documented similar waning and degradation in the regional cryospheric environment during the 20th century (Belmonte Ribas and Marcén, 2010; Kern et al., 2007, 2008; Mihevc, 2009).

Beside the mass balance fluctuations chemical stratigraphy is usually also regarded to carry valuable environmental information in glacial ice bodies. However, the small temperate glaciers of the Balkans and of the entire Mediterranean region are characterized by relatively warm ice and firn temperatures and high amount of melt water percolation (Grünewald and Scheithauer, 2008, 2010). Hence melt water induced relocation as a dominant post-depositional process in this environment severely destroys the original chemical information (Eichler et al., 2001) similarly to findings from many tropical and subtropical ice core studies (e.g. He et al., 2001; Thompson, 1980). Not like for superficial ice deposits where glacier ice develops via snow metamorphosis (e.g. Paterson, 1994) in the subterranean conditions a usual way of ice formation is freezing directly from water (Luetscher, 2004, 2005; Mavlyudov, 1989, 2008). In this case ice deposit is built from massive congelation ice; the melt water appearing in the ablation season runs off on the surface of the ice block so infiltration as post-depositional process does not take place.

In this situation particular cave ice deposits in the Mediterranean mountain ranges, those where the role of firnification is negligible in the ice formation, offer a unique alternative to decipher comparable palaeoenvironmental information (e.g. air pollution history) like Alpine glaciers (Schwikowski, 2004).

In the framework of a joint Croatian-Hungarian bilateral research project we investigate the perennial ice accumulations to evaluate the potential of the preserved glaciochemical signal in reconstruction of past climate and pollution history.

2 Description of the cave

Vukušić Ice Cave (Vukušić snježnica, 44.8° N, 14.98° E 1470 m a.s.l.) is located near the Zavižan Peak in the northern part of the Velebit Mountain, in the Croatian part of the Dinaric karst (Fig. 1). Vukušić Ice Cave consists of an entrance part and two chambers. These chambers are connected with upper entrance through the shaft. Two cave chambers are field with permanent cave ice. Length of the cave is 20 m and hosted in the Middle Jurassic (Dogger) limestone. Depth from the upper entrance to the ice level is 30 m and from the ice level to the bottom is ∼ 15 m more (45 m in total).

There have not been available year-round ventilation data yet, however the system is thought to be classified as static cave with congelation ice (Luetscher and Jeannin, 2004).

The first documented cave survey was made in 1962 (SDH, 1962). The ice floor filled completely (i.e. wall-to-wall) the main chamber at that time (Fig. 2). The ice surface eroded ∼ 20 cm until 2007 (Kern et al., 2008) and eroded further 6 cm until late autumn of 2008. Total ice area is only ∼ 50 m^2 and the volume of the ice block is estimated to 550–750 m^3. Detailed survey of the deeper sector of the cave is still missing.

3 Materials and methods

3.1 Sample acquisition and sample handling

3.1.1 Ice drilling

Two drill cores (Ø = 3 cm, length: 2.4 m and 26 cm) were extracted from the ice deposit on 28 October 2008. The drilling sites were positioned on the flat surface of the ice block (Fig. 2). The level of the ice was anchored before the coring procedure and all depth data is referred, uniformly, as depth below the 28 October 2008 ice surface.

The deepest 40 cm long section of the 2.4 m long ice core and of the total 26 cm long ice core were kept as one sample and labelled as VS_upper and VS_lower, respectively, and put into dried plastic bottles (V = 1 L).

The upper 2 m long segment of the 2.4 m long ice core was partitioned into 36 sections. Subsamples were labelled from VS1.1 to VS4.6 and VS6.1 to VS7.6 starting from the surface of the ice body. The VS5.X code was skipped as the fifth run stuck into a frozen branch and only few cm wood chips were in the auger. This wood was situated in a muddy ice layer. Limestone fragments up to 2 mm and, unusually, dark organic rich material were observed in three consecutive samples VS4.6, VS6.1 and VS6.2 corresponded to the 1.24–1.39 m depth range. Mean sample length is ∼ 5.32 cm and the variability is modest between the samples ranging from 5 to 5.67 cm.

No any fluid was used during the drilling process to minimize contamination (Boutron and Batifol, 1985). In addition rinsing techniques on ice cores were also avoided and mechanical decontamination was applied (Boutron and Batifol, 1985). Mechanical decontamination was established as outermost 2 mm ice was peeled from each core using clean and dry plastic knife. Separate knives were used for each sample. Core processing was prepared in plastic gloves and plastic gloves were washed by distilled water between each different core and dried by swiping with clean paper wadding.

Each subsample was put into a clean and dry standard 50 ml centrifuge tube sealed and stored into insulated box and kept frozen until transported to the laboratory. Plastic knives and tubes had been precleaned with ultrapure water in the laboratory, dried and kept clean until sampling.

3.1.2 Sample treatment in the laboratory

In the laboratory all samples were melted completely to affirm the isotopic and elemental homogeneity of the samples. The samples were filtered using Watman2 syringe filter. Afterwards 12 mL of water sample was pipetted into plastic vials and stored in fridge for stable isotope analysis and 100 µL distilled concentric nitric acid (Merck, Germany) was added to the rest of the samples for the fixation of the elements in liquid

phase and also stored in fridge. All material assumed to contact with the samples had been carefully precleaned with ultrapure water in the laboratory.

3.2 Tritium measurements

Tritium (^{3}H) activity of VS_upper and VS_lower samples were analysed at the Laboratory for Measurements of Low-level Radioactivity, Ruđer Boškovic Institute. Tritium in water samples was measured in liquid scintillation counter (LSC) Quantulus 1220 using electrolytic enrichment of water samples prior the measurement. System of electrolytic enrichment consists of 20 cells of 500 mL volume and equipments for primary and secondary distillations. Final volume of water sample after electrolysis is 19 ± 1 mL. The average enrichment factor is 20 ± 1. Mixture of 8 mL of enriched water and 12 mL of scintillation cocktail Ultima Gold LLT in plastic vials is used for counting in LSC. Results are reported in tritium units (1 TU is 0.1183 Bq L^{-1}) (Curie, 1995). The limit of detection is 0.3 to 0.5 TU, depending on the measurement duration.

3.3 Radiocarbon dating

Four outcropping wood macro-remnant (branch, trunk) were sampled from the overhanging ice wall and one was penetrated by the auger at 1.4 m below the actual ice surface (see Sect. 3.1.1). The deepest accessed sample (∼ 4.2 m below the surface) was dated by radiocarbon method.

Radiocarbon activity of wood sample for ^{14}C dating was also measured by LSC Quantulus 1220 using benzene synthesis method for sample preparation (Horvatinčić et al., 2004) at the Laboratory for Measurements of Low-level Radioactivity, Ruđer Bošković Institute. CO_2 obtained by combustion of wood, in the reaction with lithium at 700 °C–900 °C produce lithium carbide which is subsequently hydrolyzed to acetylene by adding distilled water. Trimerisation of acetylene to benzene is performed on the vanadium catalyst.

Calibration of ^{14}C ages were performed using the OxCal v3.10. software (Bronk Ramsey, 2001) on IntCal04 (Reimer et al., 2004) dataset.

3.4 Stable isotope analysis

Stable oxygen and hydrogen isotope measurements were carried out according to the ideas of CO_2-H_2O equilibration (Epstein and Mayeda, 1953) and H_2-H_2O equilibration by Pt-catalyst (Posser and Scrimgeour, 1995). The equilibrated CO_2 and H_2 gases were measured by a Finnigan delta plus XP mass spectrometer in continuous flow mode at the Institute for Geochemical Research, Hungarian Academy of Sciences.

Stable isotope compositions are expressed in the conventional delta notation (McKinney et al., 1950):

$$\delta = (\ - R_{std})/R_{std} \times 1000\ [‰]\ \text{VSMOW},$$

where R and R_{std} are $^{18}O/^{16}O$ or $^{2}H/^{1}H$ ratios in the sample and in the standard (Vienna Standard Mean Sea Water = VSMOW), respectively. Two-point linear normalization was applied to determine the final results (Paul et al., 2007). The uncertainties of the stable isotope data are ± 0.2‰ and ± 2.0‰ for oxygen and hydrogen, respectively.

Deuterium excess (d-excess) was calculated as $d = \delta D - 8 \times \delta^{18}O$ (Dansgaard, 1964).

3.5 Chemical composition of the cave ice

The element content was determined using a Thermo-Finnigan Element2 Magnetic Sectorfield ICP-MS at the Institute of Isotopes of the Hungarian Academy of Sciences. Samples were analyzed along with blank samples.

Optimal instrument operation parameters were: RF power; 1340 W, cooling gas flow rate; 15.4 L min^{-1}, auxiliary gas flow rate; 1.01 L min^{-1}, nebulizer gas flow rate;

0.965 L min^{-1}, solution uptake rate; 100 µL min^{-1}, resolution (m/Δm); 300, mass window; 5, samples per peak; 200, search window; 60, integration window; 300, integration type; 5 × 5.

Sample introduction was performed by ASX-520 Autosampler (Cetac), conical nebulizer (1 mL min^{-1} sample flow rate) and Scott-type spray chamber under class 100 000 clean room conditions. Limit of detection (LOD) was 0.01 ng g^{-1}. Forty-five chemical species were screened and 33 presented results above the detection limit at least in one sample out of the 36 analysed ice core samples, however only 17 elements was detected in each ice sample.

The main modes of common variability among elements a principal component analysis (PCA) (Jolliffe, 2002) was carried out. Component loadings (eigenvectors), which display the pattern of association of elements with each component, were employed to detect groupings in the ice core chemistry. PCA, using statistiXL v 1.7 beta, was established on the subset of the 17 elements those were detected in each ice sample. Only PCs with eigenvalue > 1 were regarded. In addition, pair-wise correlation analysis was also performed for the elemental concentration series to track similarities also for the element with some gaps (i.e. concentration < LOD) in the depth profile. To avoid major bias due to very few data point only those elements were involved into the correlation analysis that was detected at least in 20 samples.

3.6 Climatic setting of the area and reference data from the local precipitation

The instrumental reference data could be obtained from the nearby meteorological station (Zavižan 44.82° N, 14.98° E, 1594 m a.s.l.). The distance between Zavižan station and the ice cave is only 1500 m in the NW direction. The annual course of climate (Fig. 3a) and the long-term interannual, decadal variability (Fig. 3b) over the region, including the Vukušić Ice Cave, can be perfectly characterized on the basis of Zavižan data. Briefly, temperature follows a typical annual cycle, the coldest months are January and February, when mean monthly temperature is −4 °C. The warmest months

are July (12.4 °C) and August (12.6 °C). The long-term (1958–2009) mean annual precipitation total is fairly high (1950 mm). The seasonal course presents two maxima: a minor one in April and a major one in November. Generally one-third of annual precipitation falls between October-December. The driest month is July when the monthly precipitation total was below 100 mm in 33 cases between 1958 and 2009 and among these were 11 years when the July precipitation was less than 40 mm.

The long-term precipitation variability do not show any trend, however some cyclic variation of wet and dry periods appears as a consequence of the North Atlantic Oscillation impact on regional precipitation (Tošič, 2004). In contrast the long-term temperature series present increasing trend, and the temperature rise is more pronounced in the summer season. The rising summer air temperature has already been reported from many sites over the region (Saaroni et al., 2003; Xoplaki et al., 2003).

Tritium activity and stable isotopes (Horvatinčić et al., 2005; Vreča et al., 2006) had been monitored in the precipitation at Zavižan station between September 2000 and December 2003. Chemistry of precipitation have been monitoring since 1981 (EMEP, 2008; Špoler Čanić et al., 2009). Calcium and Mg were measured both in the local precipitation and from the cave ice core of Vukušić Ice Cave so they provided an opportunity to compare mean concentrations and relative abundance. The precipitation water chemistry data were updated to 2009 (Sonja Vidič, personal commuication, 2010). Past tritium activity of Zagreb and Vienna was also used as regional reference series from the ISOHIS database (IAEA, 2004) in evaluation of the tritium concentration values derived from the cave ice. Decayed tritium activity was calculated for the date of measurement of cave ice samples using the half-life as 12.32 years (Lucas and Unterweger, 2000).

4 Results and discussion

Results of the stable isotopic analyses and the element concentration data of the 36 cave ice samples are archived as Supplementary Online Material (SOM).

4.1 Results of the age determinations

The results of tritium measurements from the VS_lower and VS_upper samples are 1.8 ± 0.5 TU and 9.9 ± 0.6 TU, respectively. The tritium concentration of the upper sample is higher than the measured triannual amount weighted mean tritium concentration of the local recent (September 2000– August 2003) precipitation (6.75 TU). Looking at the diagrams of decay-corrected time series of past ^{3}H concentration of local and regional precipitation (Fig. 4) it is evident that the sampled ice layer deposited from precipitation fallen at an earlier period. The nearest potential period, as seen from the Zagreb record, is 1991 when the fallen precipitation still could produce the ^{3}H activity measured in VS_upper sample. However we feel it unlikely, that ~ 30 cm of ice could have deposited in the early 1990s and it could be still preserved when ca. $-6\,\mathrm{cm\,yr^{-1}}$ the measured ice loss rate and the long term (1962–2007) rate of ice level change is also negative. Two additional potential periods are from early 1970s to early 1980s and some shorter interval between 1954 and 1960. Between these periods (i.e. from 1961 to early 1970s) the decay-corrected activity of the past precipitations is still estimated to be above 10 TU (Fig. 4).

The tritium activity of the lower sample is fairly low but definitely higher than the pre-1953 level could be. Since the natural level of tritium in the Central European precipitation was around 5 TU (Roether, 1967); which have already decayed to ~ 0.1 TU level, and severely elevated atmospheric tritium concentration, a "by-product" of atmospheric thermonuclear weapon tests, appeared in the European precipitation from ~ 1953 (Eriksson, 1965). So the measured ^{3}H activity of the VS_lower sample suggests mixed sample of pre-bomb (< 0.1 TU) and post-bomb ($> \sim 10$ TU) precipitation. As a conservative approximation it can be estimated that the ice accumulated from the precipitation fallen between 1950 and 1955.

Radiocarbon dating derived conventional date is 197 ± 50 BP yr, calibrated age ranges for the $1\,\sigma$ probability are 1640–1690 (17.7%), 1730–1810 (39%) 1920–1960 (11.5%) (Fig. 5).

4.2 Stable isotopic features of the cave ice

Stable isotopic data of the 36 cave ice samples range from −11.97‰ to −8.02‰ and from −82‰ to −53.1‰, for $\delta^{18}O$ and δD, respectively. The relationship of $\delta^{18}O - \delta D$ data can be described by the equation of the best fit line, the so-called water line (Fórizs, 2005; Rozanski et al., 1993). Derived water line of the Vukušić ice core $\delta D = 7.80\,\delta^{18}O + 11.56$ agrees remarkably well with the water line of the local precipitation (Fig. 6) derived from the Zavižan record ($\delta D = 8.00\,\delta^{18}O + 16.01$) following outlier correction (Kern et al., 2008). This is solid evidence that the ice is originated from the local precipitation and perfectly preserved the relative ratios of the different water isotopes.

The amount weighted mean values of $\delta^{18}O$ and δD of the Zavižan precipitation are −9.68‰ and −63.1‰, respectively, calculated for the September 2000–August 2003. The corresponding summer (−7.79‰, −44.9‰) and winter (−11.90‰, −82.0‰) seasonal mean values nicely bracket the fluctuations of cave ice stable isotopes (Fig. 7). Similar observation was reported by Luetscher et al. (2007) who interpreted it as preserved seasonal isotopic cycles. However in the case of Vukušić ice core we hardly imagine that the found signal is an intra-annual variability.

The cave ice data tend to be closer to the winter and shove off the summer mean values. There is a sole sample (VS6.3 at 1.42 m) that approaches the summer mean level. This tendency appeared from another aspect when the mean isotopic data of the cave ice (−9.94‰, −66.0‰) were compared to the local amount weighted atmospheric precipitation (−9.66‰, −62.87‰). It is evident that the mean isotopic values of the cave ice are more depleted than the mean precipitation.

This composition suggests that the least depleted rains of the year, which are expected to fall during summer, do not take part in the aggradation of the cave ice. The amount weighted mean isotopic composition of the non-summer month (i.e. from September to May; −9.94‰, −65.6‰), is almost identical with the mean isotopic data of the cave ice.

The *d*-excess values of the cave ice samples range from 9.7 to 18.1, the mean value is 13.5 (SOM). This is again in line with the regional isotope hydrological characters of the precipitation (Vreča et al., 2006).

The ∼3 yr long record of local precipitation is fairly short to state that the found correspondence is a solid evidence for the absence of the summer precipitation in the Vukušić ice core and the fine preservation of the precipitation of the complementary season however reinforces the model.

It is interesting to compare the stable isotopic characteristics of Vukušić ice core to similar data from the cave ice of the neighbouring Ledena Pit (Jelenić al., 2001). It was suggested that in the Ledena Pit the precipitation from winter half year plays also more dominant role in the ice formation than the summer half year (Horvatinčić, 1996; Kern et al., 2008). The distance of the caves is only 1.5 km, so the isotopic composition of the precipitation input is surely the same at the two caves. The water line of the cave ice from Ledena Pit is significantly different ($\delta D = 5.48 \times \delta^{18}O - 11.79$) (Horvatinčić, 1996) from the water line derived from the Vukušić ice core. Ledena Pit's cave ice water line clearly presents isotopic evidence for post-depositional processes accompanied by kinetic fractionation (Kern et al., 2008; Lacelle et al., 2009).

The contrasting isotopic characteristics of the two cave ice, fed by the same local precipitation, can be plausible explained by the differences in their glaciological systems. Ledena Pit's ice deposit is a classical example of snow fed and firnified cave deposits. Melting/refreezing cycles of the snow/firn accumulation are highly probable to take place repeatedly. The Ledena Pit's system is similar to warm glaciers inasmuch as snow/firn can sublimate into the cave atmosphere triggering a strong kinetic fractionation. Melt water from the surface or even from deeper layers can also easily escape from the sponge-like structure of the firn. These processes can skew the $\delta^{18}O - \delta D$ relationship of the residual snow/firn. The Vukušić Ice Cave is a much simple system. The melting process could affect only the surface of the ice block. There is no possibility to infiltrate into the dense congelation ice. However the melt water flows away from the ice surface. The fact that there has never been observed any lake or pond on

the surface of Vukušić's ice block like in other caves (Perşoiu, 2004; Kern et al., 2009) further underpins that the melted water rapidly escape from the ice surface.

Above results reinforce a simple galciogenetic model for the Vukušić Ice Cave where the congelation ice once deposited conserves the original composition until erosion.

4.3 External and internal signals in the cave ice chemical record

The element concentrations and the correlation matrix are presented as Supplementary On-line Material.

The first three PC's eigenvalue exceeded 1, the chosen threshold, and they explained the 84.65% of the total variance (Fig. 8). PC1 explained more than half (59.58%) of the full variance. The score coefficients reveal that from the more abundant elements Mg and Ca obtained highest scores on PC1 (Fig. 8). However, Ti, Mn, Sr presented only slightly smaller scores. In addition most of the studied trace elements (mean concentration <5ng g^{-1}) like B, Rb, As, Mo, Co had also the highest score on PC1.

The characteristic members of this group (Ca, Mg, Sr) are typical trace elements in a limestone hosted cave (e.g. Fairchild and Treble, 2009). As was expected, the cave ice samples contained much more Ca and Mg than the long term (1981–2009) mean concentration of Ca and Mg in Zavižan precipitation (Table 1.). This high enrichment of Ca and Mg in cave ice has been also observed in an Italian ice cave (Citterio et al., 2004a). In addition the Ca/Mg ratio in the annual precipitation at Zavižan ranged between 1.5 and 12 with median value of 5.6 whereas in the cave ice it ranged between 29 and 98 with median value of 50.8. We argue that beside their higher concentration the large difference in the Ca/Mg ratio between the precipitation and the cave ice provides also good evidence that the Ca and Mg is not from the atmospheric deposition, but they arrived from the local karstic bedrock. Finally, the characteristically elevated concentration values (Fig. 9) of the elements in this group fit perfectly to the depth of the muddy layer with limestone fragments observed in the core (see Sect. 3.1.1).

Taking all together it is fairly sure the fluctuation of PC1, governed by Ca and Mg and Sr indicates the karstic contribution.

The most characteristic element of this group is Ca. We think that the Ca concentration in other cave ice sequences could be also regarded as the indicator of bedrock derived (internal) components. This might be a useful approach also for other studies dealing with chemistry of cave ice (Citterio et al., 2004b; Clausen et al., 2007).

It seems logical to state that the trace elements that are strongly correlates with the PC1 karst-group (e.g. Ti, B, U) should also come from the karstic bedrock. Exclusively those elements that have not shown significant positive correlation with this Ca-group could come from a different source than the local bedrock and more probably these could have atmospheric origin and might preserve some information about the past deposition history.

Among the elements with higher concentration Zn obtained the highest score on PC2 (Fig. 8). Copper and Cr also had high (even higher than Zn) scores on PC2. They tend to show higher concentrations near the surface. Similar trend was observed for Ag, but it was not included into the PCA because only 10 subsamples provided detectable concentration data, however 9 of these gathered in the upper 0.6 m of the core and followed Zn and Cu. The members of this group suggest some industrial (e.g. non-ferrous smelter) source.

Although we still could not find information about the past deposition rates of these metals and metalloids, so we lack the real verification, it is interesting to note the national emission inventory (Poljanac et al., 2010) documents increasing emission for Cu and Zn. The ice core derived trends agree with these emission trends. In the lack of local deposition reference we have compared the mean concentration values of these elements to two Alpine datasets (Barbante et al., 2004; Gabrielli et al., 2008) (Table 1). The mean concentration values for Cr and Cu agrees very well with the Alpine data. However in the case of Zn the cave ice exhibited higher concentration by an order of magnitude. The above mentioned national increasing Zn emission can be responsible for this enhanced Zn deposition.

Aluminium and Fe obtained the highest scores on PC3 (Fig. 8). Mean concentration of Fe from this Croatian cave ice agrees fairly well with the mean value reported from the Dolomites for the 1997/1998 winter (Table 1). Probably these components carry the signal from the distal (beyond the karstic domain) crustal source and an anthropogenic (at least one) source (different from Zn-group).

5 Conclusions

Two ice cores were extracted from the perennial subterranean cave ice deposit of Vukušić Ice Cave, Velebit Mt. These ice cores served pilot samples to evaluate the potential of the preserved glaciochemical signal in reconstruction of past climate and pollution history. The ^{3}H activity, $^{18}O/^{16}O$ and $D/^{1}H$ ratio and concentration of 33 metals and metalloids have been analysed in the cave ice.

The tritium data suggested that the ice deposition at 2–2.4 m depth is build from precipitation fallen ∼45 years before sampling and the uppermost ice layer could be estimated between early 1970s and early 1980s or between ∼ 1954 and 1960.

Both, the fluctuation range of stable oxygen and hydrogen isotopes and the derived isotopic water line of the of the 2 m long ice core agree reasonably well with the corresponding data of the local precipitation.

Due to the native karstic environment of the cavity and the dominant karstic dissolution processes Ca can be used as a “master series” to check which chemical species have been attributed to the same (i.e. bedrock) origin.

For a cave ice environment exclusively those chemical species could preserve reliable atmospheric deposition histories that are not correlated with the Ca-group. In the present study the cave ice documented trend of enhanced deposition of Zn and Cu nicely agreed with the trend seen from the local emission inventory.

The presented results and a comparison to the nearby Ledena Pit pointed out that the potential of Vukušić Ice Cave’s ice deposit is superior for paleoclimatological studies. The next stage of the project is to establish serial datings with higher resolution to

develop sufficiently tight chronological constraints and to place the found fluctuations of the isotopic and chemical stratigraphy into temporal dimension.

Supplementary material related to this article is available online at: http://www.the-cryosphere-discuss.net/4/1561/2010/tcd-4-1561-2010-supplement.zip.

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Table 1. Basic statistics (mean and standard deviation-SD) of elemental concentrations measured in the samples of Vukušić ice core. If concentration of particular element was below Limit of Detection (LOD) in particular sample then LOD/2 was used in calculation of the mean concentration. However, to avoid major bias due to this artificial substitution only those elements are presented for that no more than four samples were below LOD. Each value is in ng g^{-1}. Mean concentration values in the local precipitation and from two Alpine dataset are included as comparison.

	Vukušić ice core		Zavižan	Colle Gnifetti[b]	Dolomites[c]
	Mean	SD	precipitation[a]		
Ca	7339.40	9506.19	1.57		
Mg	179.18	301.42	0.32		
Al	71.23	57.13			
Zn	43.59	32.30		3.176	3.5
Ti	43.49	55.23			
Fe	31.76	18.87			27.3
Mn	19.49	53.58			
Sr	7.53	9.53			
B	3.28	5.74			
Rb	1.11	2.37			
Pb	0.69	2.76			
As	0.50	0.69			
Cu	0.31	0.42		0.412	0.72
Cr	0.29	0.26		0.35	0.1
Mo	0.20	0.29			
U	0.09	0.15			
Co	0.08	0.10			
Zr	0.06	0.06			
Ce	0.04	0.02			
Cd	0.03	0.01			

[a] Long-term mean concentration of annual mean values of local precipitation from 1981 to 2009 (EMEP, 2008).

[b] Mean concentration in the ice core section dated after 1970 (Barbante et al., 2004).

[c] Mean concentration in snow fallen from December 1997 to April 1998 at 21 sites at altitudes ranging from 1000 to 3000 m in the Dolomites (Gabrielli et al., 2008).

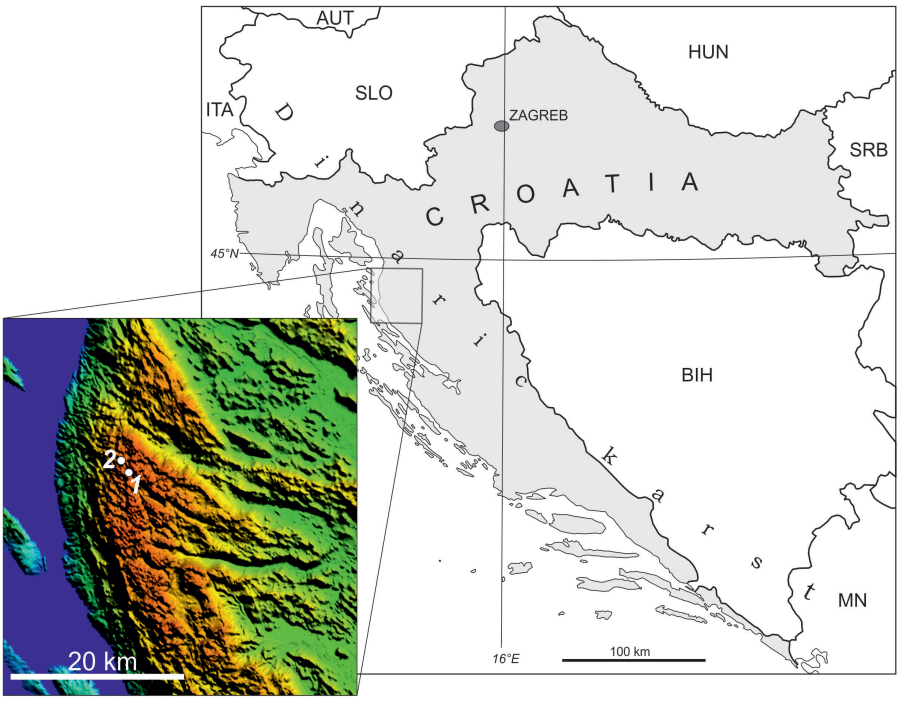

Fig. 1. Location of the Vukušić Ice Cave (1) and the Zavižan meteorological station (2).

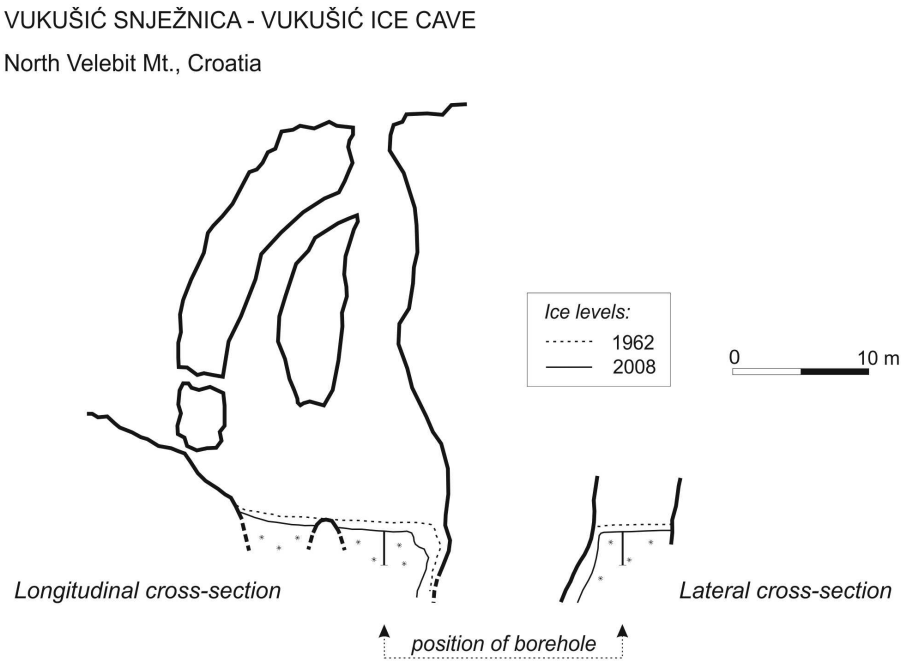

Fig. 2. Sketch of Vukušić Ice Cave (form Kuhta 2002) with lines mark the ice level at the given date (according to SDH 1962 and recent observations). The ice core locations are indicated by black arrows.

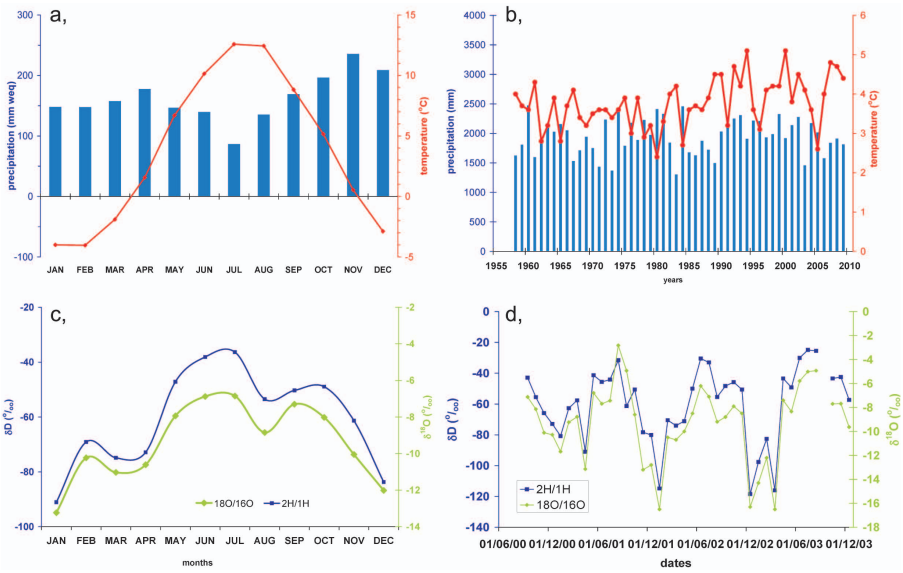

Fig. 3. Seasonal and interannual characteristics of climate and isotopes in precipitation at Zavižan. **(a)** monthly mean temperature (line) and precipitation totals (bar) calculated for the 1958–2009 period. **(b)** mean annual temperature (line) and precipitation totals (bar)over the 1958–2009 period. **(c)** monthly amount weighted stable oxygen (green) and hydrogen (blue) isotopic composition of precipitation calculated over the September 2000–December 2003 period. **(d)** monthly stable oxygen (green) and hydrogen (blue) isotopic composition of precipitation over the September 2000–December 2003 period.

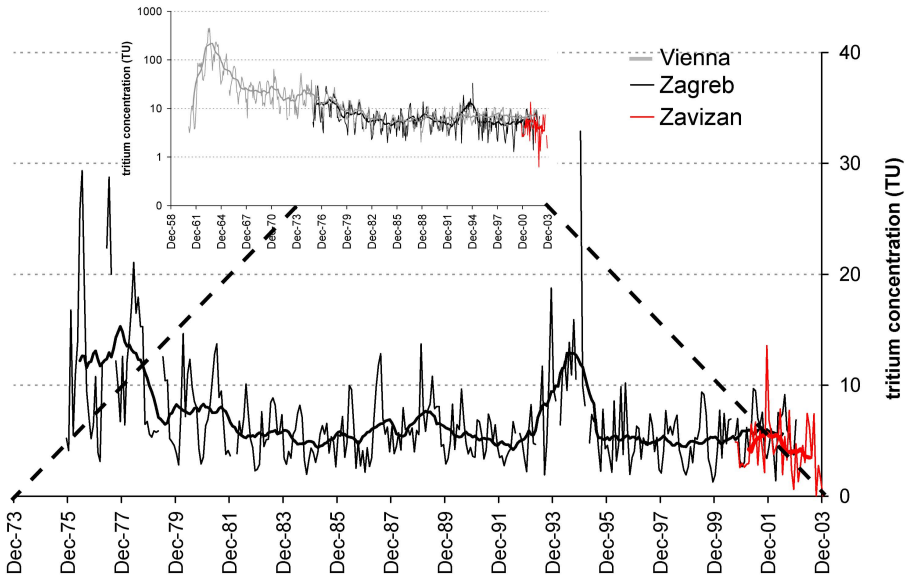

Fig. 4. Decay-corrected tritium activity of past precipitation at Zavižan (red) and Zagreb (black) over the 1973–2003 interval. The inset figure shows the same graphs completed with Vienna (gray) as the longest regional record. Thin lines show the fluctuation of monthly values, thick lines (12-month moving average) emphasize the annual variability.

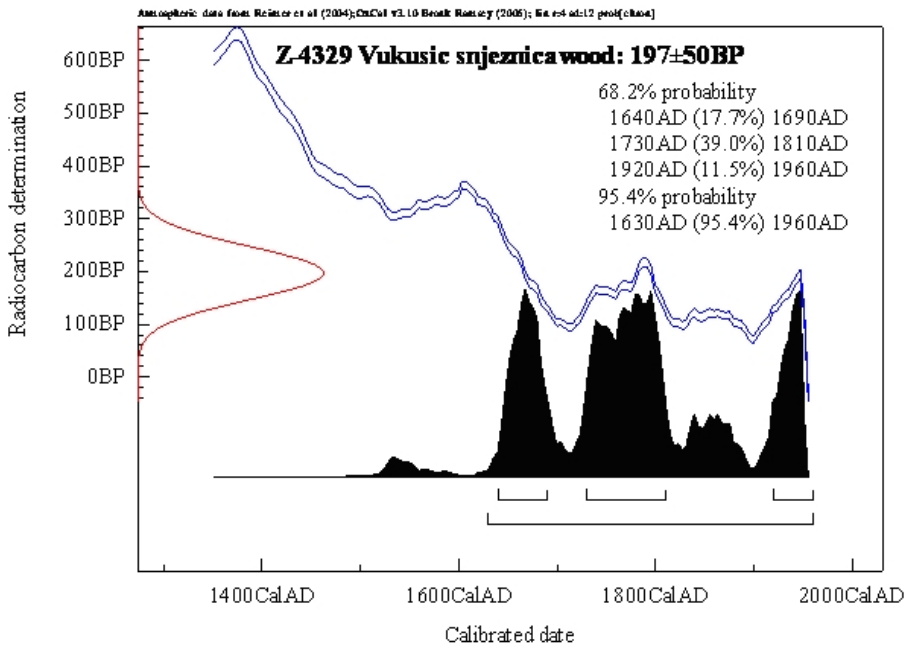

Fig. 5. Calibration of radiocarbon date of the wood sample excavated from the side wall of Vukušić Ice Cave at the depth of ~ 4–4.2 m below the 28 October 2008 ice surface.

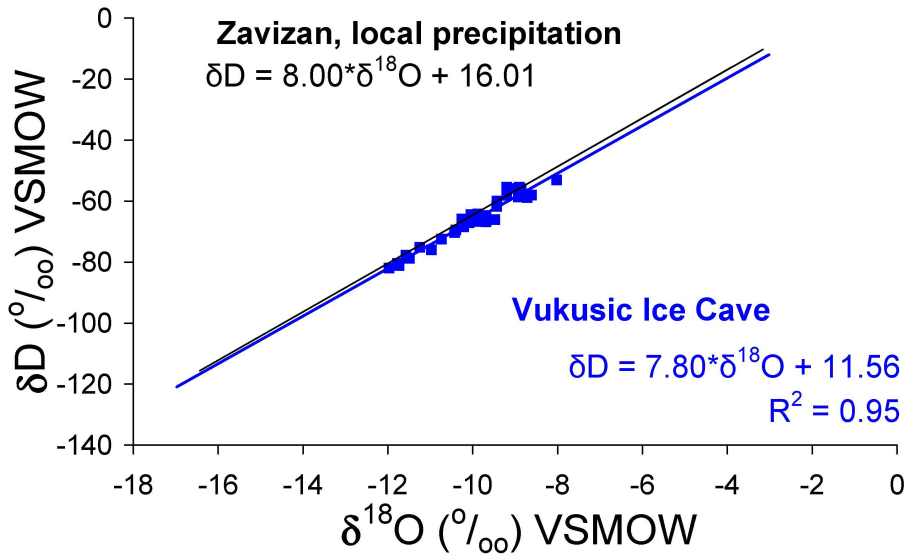

Fig. 6. Isotopic composition of the cave ice samples from the ice core of Vukušić Ice Cave (blue squares). The best-fit line and its equation with the coefficient of determination are shown by the same colour. The local meteoric water line for Zavižan precipitation and the equation are also shown (black) for comparison.

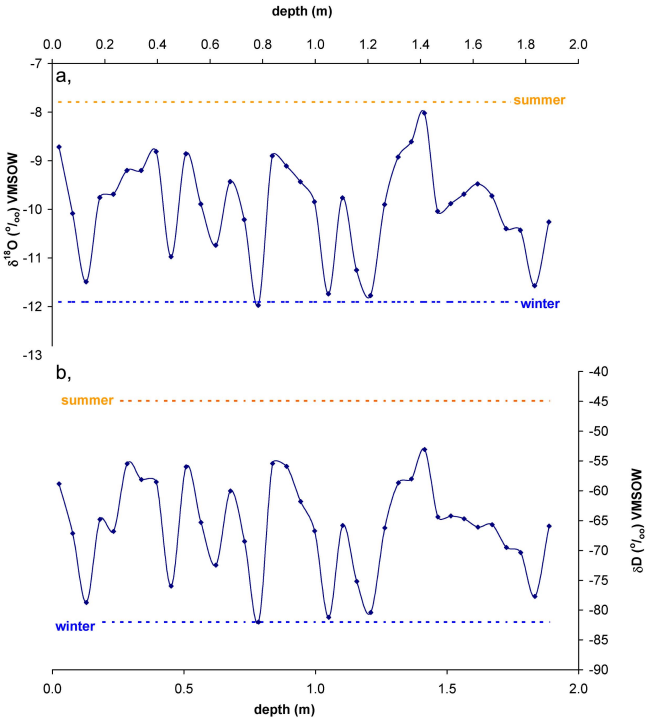

Fig. 7. The fluctuation of the stable oxygen **(a)** and hydrogen **(b)** isotopic composition of ice deposit in Vukušić Ice Cave measured along the 2 m long core profile. The corresponding amount weighted mean summer (orange) and winter (blue) values of the local precipitation for both isotopes are indicated. The seasonal mean values are estimated from the Zavižan record monitored between September 2000 and December 2003 (see Fig. 3d).

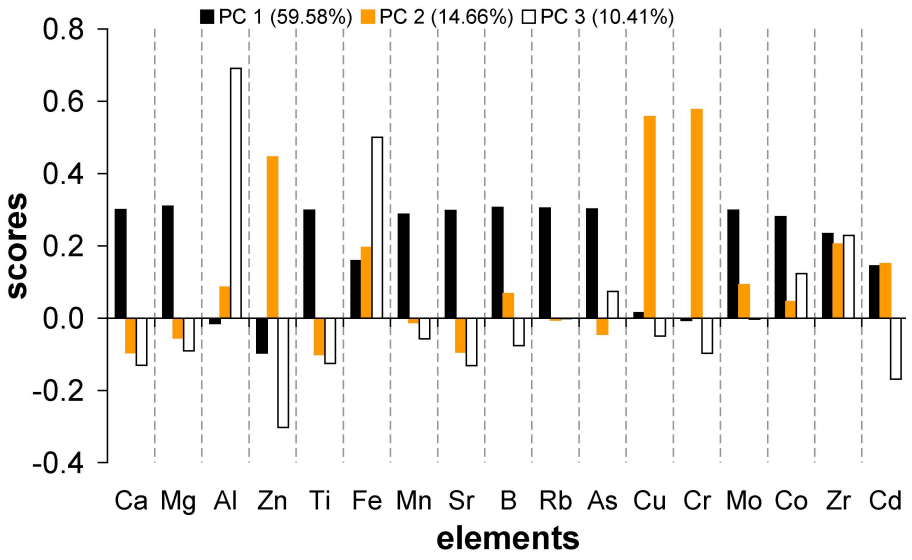

Fig. 8. Score coefficients of principal component analysis are presented as bars with height proportional with the value of the coefficient. Variance distribution of the first three extracted PCs is indicated after each between parentheses in the legend.

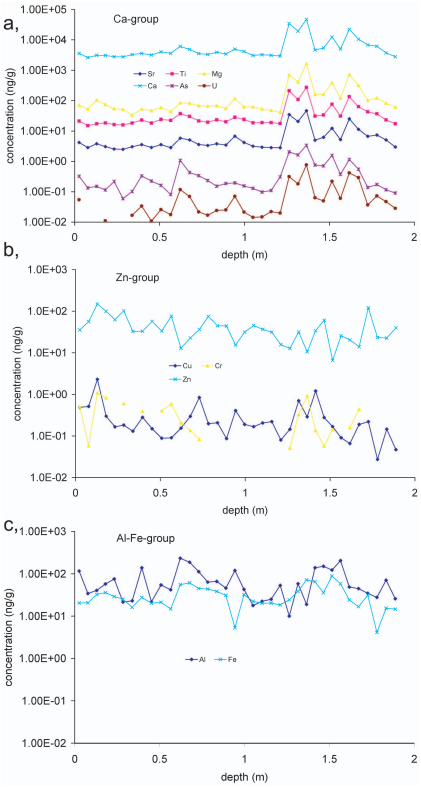

Fig. 9. Concentration profiles of the characteristic elements attributed to the three leading principal components of the glaciochemical record of the cave ice core. PC1 **(a)**, PC2 **(b)** and PC3 **(c)**.